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# Predicting Real Optimized Materials: A New Multi-Scale Approach Enabling Ultra-Long Timescale Dynamical Simulation and Optimization of High Energy Density Materials

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## DISCLAIMER



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# PREDICTING REAL OPTIMIZED MATERIALS:

## A New Multi-Scale Approach Enabling Ultra-Long Timescale Dynamical Simulation and Optimization of High Energy Density Materials

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WHITE PAPER

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## I. Introduction

The design and synthesis of novel new high energy density materials (HEDM) is more art than science. Many potential molecular systems have been identified computationally. Most computational studies are performed using traditional gas-phase quantum chemistry methods, which determine high-energy structures of a particular cluster of atoms that are geometrically constrained. At first, a minimum energy optimization of the molecular structure is sought. Once located, the adiabatic stability to decomposition via several channels is explored by locating energy barriers to decomposition. These calculations could then suggest whether a particular cluster is stable and is a viable HEDM candidate. This computational procedure offers nothing in way of practical steps about the synthesis of the HEDM molecule starting from currently existing materials, and therefore is disconnected from experimental undertakings for the realization of novel HEDMs.

We propose to apply a new multiscale simulation method for the study of shocked high energy density materials enabling, for the first time, the elucidation of chemistry under shock conditions on the 100 ps timescale. (E. J. Reed, L. E. Fried, J. D. Joannopoulos, Phys. Rev. Lett. 90, 235503 (2003)) The method combines molecular dynamics and the Euler equations for compressible flow. The method allows the molecular dynamics simulation of the system under dynamical shock conditions for orders of magnitude longer time periods than is possible using the popular non-equilibrium molecular dynamics (NEMD) approach. A computational speedup of $10^5$ has been demonstrated for an example calculation for a silicon model potential. Computational speedups orders of magnitude higher are possible in the study of high energy-density materials at the condensed phase, enabling the computational simulation and optimization of these materials for the first time. Our finding will guide experimental realization of such materials by providing the exact thermodynamical variables for the existence of such materials. Proposed systems of study include polynitrogen, oxygen, and their mixtures.

## II. Methodology

The popular non-equilibrium molecular dynamics (NEMD) approach to atomistic simulations of shock compression involves creating a shock on one edge of a large system and allowing it to propagate until it reaches the other side. The computational work required by NEMD scales at least quadratic ally in the evolution time because larger systems are needed for longer simulations. When quantum mechanical methods with poor scaling of computational effort with system size are employed, this approach to shock simulations rapidly becomes impossible. Such quantum mechanical methods like tight-binding and density functional theory are required to accurately simulate the complex chemistry that occurs in shocked high energy density materials.

The new method outlined here circumvents these difficulties by requiring simulation only of a small part of the entire system. The effects of the shock wave passing over this small piece of the system are simulated by dynamically regulating the applied stress, which is obtained from a continuum theory description of the shock wave structure. Because the size of the molecular

dynamics system is independent of the simulation time in this approach, the computational work required to simulate a shocked system is nearly linear in the simulation time, circumventing the scaling problems of NEMD.

The propagation of the shock wave is described by the 1D Euler equations for compressible flow. These equations represent conservation of mass, momentum, and energy everywhere in the material. Shock wave solutions of these equations that propagate at a constant speed $v_s$ have the form,

$$u = v_s\left(1 - \frac{\rho_0}{\rho}\right)$$

$$p - p_0 = v_s^2 \rho_0 \left(1 - \frac{\rho_0}{\rho}\right)$$

$$\varepsilon - \varepsilon_0 = p_0\left(\frac{1}{\rho_0} - \frac{1}{\rho}\right) + \frac{v_s^2}{2}\left(1 - \frac{\rho_0}{\rho}\right)^2$$

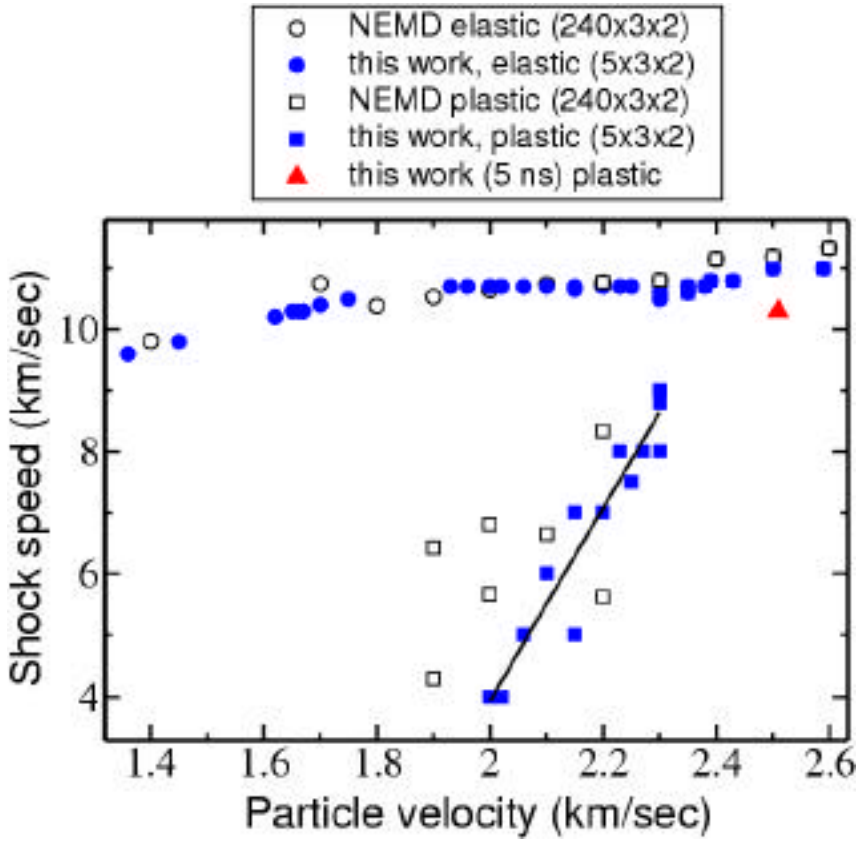
where $u$ is the local speed of sound in the laboratory frame (particle velocity), $v$ is the specific volume, $\rho = 1/v$ is the density, $e$ is the energy per unit mass, and $p$ is the negative component of the stress tensor in the direction of shock propagation, $-\sigma_{xx}$. Variables with subscript 0 are the values before the shock wave, and we have chosen $u_0 = 0$, i.e., the material is initially at rest in the laboratory frame.

For the molecular dynamics simulation, we employ the Lagrangian,

$$L = T\left(\{\dot{\vec{r}}_i\}\right) - V\left(\{\vec{r}_i\}\right) + \frac{1}{2}Q\dot{v}^2 + \frac{1}{2}\frac{v_s^2}{v_0^2}\left(v_0 - v\right)^2 + p_0\left(v_0 - v\right)$$

where $T$ and $V$ are kinetic and potential energies per unit mass, and $Q$ is a masslike parameter for the simulation cell size. It can be shown that the equations of motion of this Lagrangian reproduce the shock solutions of the Euler equations above. Simulation of a shock wave is accomplished by specifying a shock velocity $v_s$ and the initial thermodynamic state of the system, then performing a molecular dynamics simulation according to the Lagrangian above. Shock compression occurs automatically and all the ensuing dynamical phenomena including chemistry or phase transformations are correctly treated as in NEMD.

The figure below shows a comparison of calculated shock Hugoniots for the NEMD approach and the new method described in this proposal. These data are for approximately 10 ps simulation durations. Note the ability to utilize much smaller computational cell sizes with the new method. Also included is one data point for a 5 ns simulation using this new method which would be prohibitive with NEMD requiring a factor of $10^5$ increase in computational effort.




## Applications:

The prospect of destabilizing the strong N≡N triple bond under high pressure invited several experimental and theoretical attempts to locate and characterize bulk polymeric phases. The possible existence of polymeric forms of nitrogen is of a particular interest due to the energetic properties associated with these materials. As potential high-energy density materials (HEDMs) from an abundant natural source, they become leading candidates for alternative energy storage media. To date, the only known forms of nitrogen are $N_2$ and $N_3^-$. Recently, the synthesis of the ion $N_5^+$ in a complex with $As_xF_y$ anion is an encouraging step toward the realization of these materials. Similarly, metastable, oxygen ring strained systems of $O_4$ and $O_8$ have been identified as HEDM candidates, although never realized experimentally.

In the case of nitrogen, calculations suggested polymeric regimes to exist below 100 GPa; at 70 and 50 GPa, while diamond-anvil-cell experiments failed to record a transition from the

diatomic form for pressures of up to 180 GPa. A non-static, shock compressed nitrogen experiment [Radousky, 1986 #48] recorded an anomaly at pressure above 30GPa that was later interpreted as a dissociation to dense atomic phase. These discrepancies can be alleviated through the implementation of our methodology.

We propose to implement our computational procedure to simulate shock compression of liquid nitrogen and liquid oxygen to provide the experimentally verifiable parameters for the existence of high-energy state of these systems. Simulations with varying initial thermodynamic state of these systems and the shock speeds will be conducted in order to map out the new high-energy density metastable state of these systems.

### Deliverables:

Phase 1- (18 months): Develop a parallel version of our procedure that allows its implementation with state of the art solid – state electronic structure methods to efficiently and accurately determine the properties of interest. Conduct simulations on liquid nitrogen at various thermo dynamical conditions and shock speeds to determine the pressure-temperature regime for the existence of polynitrogen phases.

Phase 2- (one year): Conduct simulations on liquid phase of oxygen, and mixtures of nitrogen-oxygen at various thermo dynamical conditions and shock speeds to determine the pressure-temperature regime for the existence of metastable phases.

## V. Funding requirements

We anticipate the following funding support

| **Name** | **Fraction of support (of the full time employee)** | **in dollars per year** |
|---|---|---|
| Evan Reed | 1.0 | $200K |
| Riad Manaa | 0.5 | $150K |
| Larry Fried | 0.2 | $60K |
| Total per year | | $410K |